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The role of the initial reagents in the low-O_2 pressure synthesis of $YBa_2Cu_4O_8$

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A comparative analysis of the effect of the starting reagents in the synthesis of $YBa_2Cu_4O_8$ (124) is presented. Eight different combinations of salts and oxides of the elements in the initial composition were studied. It is shown that all the syntheses starting with copper nitrate give 124 in approximately 80 h of treatment with only small amounts of CuO and Y_2BaCuO_5 impurities. Longer times are needed if CuO is used as a starting reagent.

1. Introduction

The $YBa_2Cu_4O_8$ (124) phase was first observed as a defect phase in the $YBa_2Cu_3O_{7-x}$ (123) synthesis process [1] and then formed as a single phase in thin films on $SrTiO_3$. Since then many bulk synthesis procedures have been developed, differing in oxygen pressure and treatment temperature.

The 124 structure (space group Ammm) is very similar to that of 123, from which it differs by an added CuO plane in the unit cell. As in the 123 phase, the critical temperature for the superconducting transition is higher than the liquid nitrogen temperature. In comparison with 123, it presents a higher oxygen stability and the absence of structural phase transitions that generate twins during the synthesis [2].

The first bulk synthesis of 124 and 247 was performed at an oxygen pressure exceeding 400 atm [3]. However, it was soon discovered that these materials could be produced at 1 atm oxygen pressure [4–11]. Low oxygen pressure synthesis is possible because at low enough temperatures (below 860 °C) the thermodynamically stable state of a mixture of 123 and CuO in a 1:1 molar ratio is the 124 compound [2, 12].

Even if low-pressure synthesis is possible, the chemical kinetics may not favour 124 phase formation. In fact, the first 1 atm oxygen pressure synthesis reported was performed starting from nitrates of yttrium, copper and barium in the presence of K_2CO_3 or Na_2CO_3, used as reaction enhancers [4]. Recent work has shown the possibility of obtaining 124 from nitrates without reaction enhancers [11]. Other simple methods start from Y_2O_3, $Ba(NO_3)_2$ and CuO powders; in this case CuO submicrometre particle size is needed to achieve good results [7]. The success of each method depends thus in a relevant way on the characteristics of the starting reagents (micromorphology and chemical nature).

124 is not only an interesting compound from a fundamental point of view, but it may also be technologically important because of its oxygen stability. Therefore, it becomes relevant to further develop synthesis procedures that allow production of this material without sophisticated high-pressure equipment, with a simple procedure (small number of processing steps) and with as few impurities as possible. Moreover, if a given procedure has to be implemented on a larger than laboratory production scale, the initial reagents should be commercially available and able to be used without a particular treatment or careful morphological selection. In this work a comparative study is presented of the reaction evolution of different combinations of starting reagents mixed in stoichiometric proportions to give $YBa_2Cu_4O_8$. All the syntheses follow the same procedure and are performed at 1 atm oxygen pressure. The reaction products are identified at several reaction steps and the relevance of the different initial reagents is discussed.

2. Experimental procedure

The starting reagents were used as they came from the supplier: no particular grinding, milling or particle size selection was performed. Since the nitrates are hygroscopic, the yttrium, barium and copper content of these initial reagents was determined by elemental analysis using a Perkin-Elmer Plasma II emission spectrometer. As a further check, the molecular weight of nitrates was also determined by total calcination to oxides. This process was followed with thermogravimetry (TG) and differential thermal analysis (DTA). These measurements were performed with a Netzsch 409 thermal analysis system. The weight loss measurements confirmed, within 4%, the data obtained with the previous technique, so a reliable molecular weight was established for all initial reagents. The weight increase due to water absorption during the initial preparation procedure was below 0.1%.

The synthesis procedure was the same for all the starting groups of reagents shown in Table I below. Appropriate amounts of the reagents (giving a Y : Ba : Cu molar ratio of 1:2:4) were carefully mixed and milled and then heated up to 820 °C at the rate of 5 °C min^{-1} in flowing oxygen; the samples were left at this temperature for 12 h. After furnace-cooling to

0022–2461

TABLE I Phases of the reaction products observed for each set of initial reagents

Case No.	Reagents	Phases after 92 h	Products
1	CuO, $Ba(NO_3)_2$, $Y(NO_3)_3 \cdot xH_2O$	$YBa_2Cu_3O_y$, $Ba_4Y_2O_7$, Y_2BaCuO_5, $BaCuO_2$, CuO	$YBa_2Cu_3O_y$, $YBa_2Cu_4O_8$, Y_2BaCuO_5, $BaCuO_2$, CuO
2	CuO, $Ba(NO_3)_2$, Y_2O_3	$YBa_2Cu_3O_y$, Y_2BaCuO_5, $BaCuO_2$, CuO, $Ba_4Y_2O_7$	$YBa_2Cu_3O_y$, Y_2BaCuO_5, $BaCuO_2$, CuO
3	CuO, $BaCO_3$, $Y(NO_3)_3 \cdot xH_2O$	$YBa_2Cu_3O_y$, Y_2BaCuO_5, $BaCuO_2$, CuO, $Ba_4Y_2O_7$	$YBa_2Cu_4O_8$, Y_2BaCuO_5, $YBa_2Cu_3O_y$, $BaCuO_2$, CuO
4	CuO, $BaCO_3$, Y_2O_3	$YBa_2Cu_3O_y$, Y_2BaCuO_5, $BaCuO_2$, CuO, $Ba_4Y_2O_7$	$YBa_2Cu_4O_8$, Y_2BaCuO_5, $BaCuO_2$, CuO, $YBa_2Cu_3O_y$
5	$Cu(NO_3)_2 \cdot xH_2O$, $Ba(NO_3)_2$, $Y(NO_3)_3 \cdot xH_2O$	$YBa_2Cu_4O_8$, CuO, Y_2BaCuO_5, $Ba_4Y_2O_7$	$YBa_2Cu_4O_8$, CuO, Y_2BaCuO_5
6	$Cu(NO_3)_2 \cdot xH_2O$, $Ba(NO_3)_2$, Y_2O_3	$YBa_2Cu_4O_8$, $BaCuO_2$, CuO, Y_2BaCuO_5, $Ba_4Y_2O_7$	$YBa_2Cu_4O_8$, $BaCuO_2$, CuO, Y_2BaCuO_5
7	$Cu(NO_3)_2 \cdot xH_2O$, $BaCO_3$, $Y(NO_3)_3 \cdot xH_2O$	$YBa_2Cu_4O_8$, CuO, Y_2BaCuO_5	$YBa_2Cu_4O_8$, CuO, Y_2BaCuO_5
8	$Cu(NO_3)_2 \cdot xH_2O$, $BaCO_3$, Y_2O_3	$YBa_2Cu_4O_8$, $BaCuO_2$, CuO, Y_2BaCuO_5	$YBa_2Cu_4O_8$, $BaCuO_2$, CuO

room temperature the resulting powders were milled and heat-treated again at 820 °C for 40 h; the heating rate was 10 °C min^{-1} and the atmosphere was oxygen at a pressure of 1 atm. This last procedure was repeated several times.

For each initial composition and at every step an X-ray diffraction (XRD) analysis was performed with a Philips PW 1830 powder diffractometer with CuK_α radiation and the relevant compounds were identified.

The sample resistance was measured with a standard four-point probe method. The contacts were made with indium spots pressed on the sample. The measurement was made with a Stanford lock-in amplifier that was also used as a voltage source (frequency = 273 Hz). The system was fully automated for data acquisition. The temperature was measured and controlled with two silicon diodes, one close to the sample and the other in the cold finger. The lowest temperature reached was 15 K.

3. Results and discussion

Almost all the reactions under consideration give 124 as one of their products. However, the reaction times and the final dominant phase are not the same. The common impurity is CuO (unreacted or produced by the oxidation of $Cu(NO_3)_2 \cdot 3H_2O$). This is a general problem when simple procedures for the 1 atm synthesis of 124 are implemented [11, 13].

It would be very cumbersome to show the detailed evolution of all the eight starting compositions under consideration through their XRD patterns, so, in the following, a description of the evolution for each group of reagents is given.

1. CuO, $Ba(NO_3)_2$ and $Y(NO_3)_3 \cdot 5H_2O$. The significant reaction product at short times (up to 92 h) is Y_2BaCuO_5 (211). After 172 h there is a consistent presence of 123. After 572 h the dominant phase is the 123. In this case, the presence of 124 is very difficult to confirm.
2. CuO, $Ba(NO_3)_2$ and Y_2O_3. The 123 compound is always present and it is the dominant reaction product after 572 h. The initial intense XRD spectral lines of 211 decrease with time; the presence of 124 is difficult to confirm.
3. CuO, $BaCO_3$ and $Y(NO_3)_3 \cdot 5H_2O$. There is a significant presence of 211 up to 172 h. After 432 h the 124 phase can be clearly identified and after 572 h it becomes the dominant phase. 123 is always present.
4. CuO, $BaCO_3$ and Y_2O_3. The presence of 211 and 123 is relevant up to 292 h but there is evidence of 124 after 132 h; the dominant phase at the end (572 h) is 124.
5. $Cu(NO_3)_2 \cdot 3H_2O$, $Ba(NO_3)_2$ and $Y(NO_3)_3 \cdot 5H_2O$. After 52 h there are strong 124 peaks; the initial presence of 211 is reduced but never eliminated even after 572 h.
6. $Cu(NO_3)_2 \cdot 3H_2O$, $Ba(NO_3)_2$ and Y_2O_3. There is no substantial difference with respect to the previous composition.
7. $Cu(NO_3)_2 \cdot 3H_2O$, $BaCO_3$ and $Y(NO_3)_3 \cdot 5H_2O$. After 52 h the dominant phase is 124. The diffractograms of the powders after 132 and 172 h did not show any variation so the treatment was not continued afterwards. The 211 compound is always present as impurity.
8. $Cu(NO_3)_2 \cdot 3H_2O$, $BaCO_3$ and Y_2O_3. In general, there is no substantial difference with respect to the previous composition. Nevertheless, this set of reagents can give a better result than the previous one because some spurious X-ray peaks are absent.

A résumé of the resulting phases after 92 h and at the end of the treatment for each case (as defined by the previous list) is given in Table I.

It is relevant to show the XRD patterns of the resulting products, for the various initial reagents, at significant time scales. Fig. 1a shows the patterns of the four starting compositions with CuO (1–4) and Fig. 1b the ones with $Cu(NO_3)_2 \cdot 3H_2O$ (5–8), both after 92 h of treatment; Fig. 2a and b show the

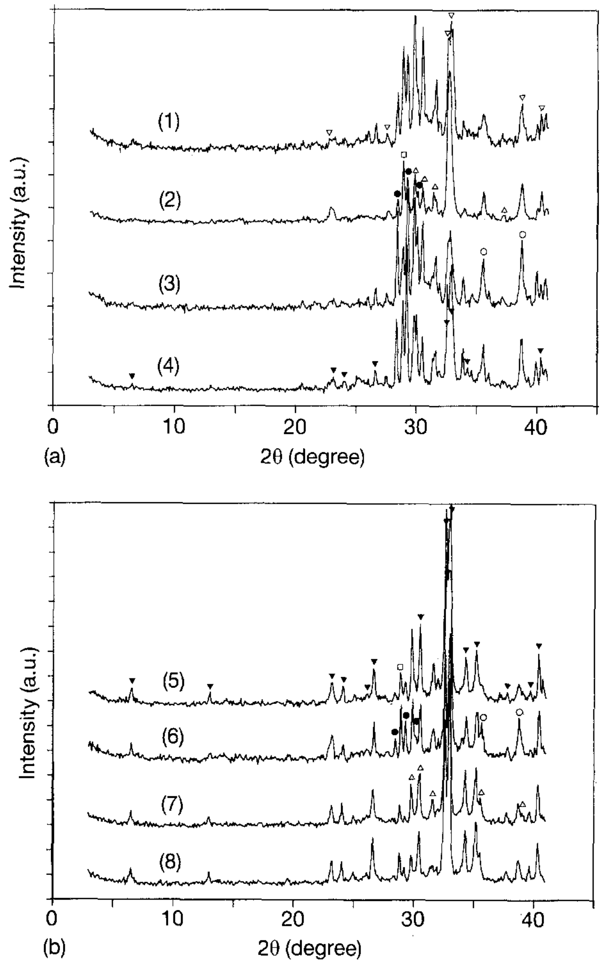

Figure 1 (a, b) X-ray diffractograms of the reaction products after 92 h of treatment. The number for each graph identifies a particular set of initial reagents (see Table I). Symbols denote the main peaks of the phases formed: (▼) $YBa_2Cu_4O_8$, (△) Y_2BaCuO_5, (▽) $YBa_2Cu_3O_7$, (□) $Y_2Ba_4O_7$, (○) CuO, (●) $BaCuO_2$.

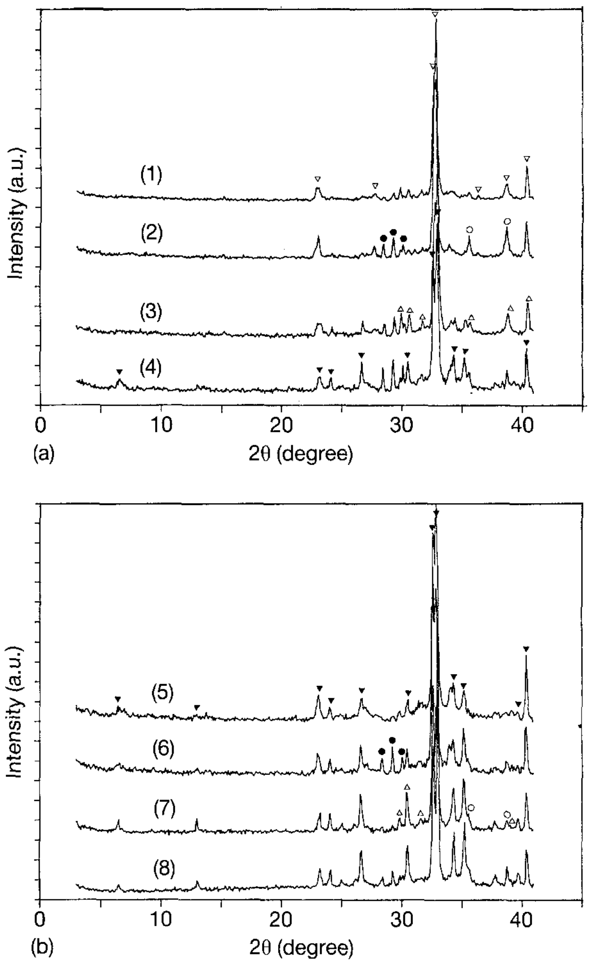

Figure 2 (a, b) X-ray diffractograms of the reaction products, at the end of the treatment, for the set of initial reagents identified with the corresponding number in Table I. Symbols denote the main peaks of the phases formed: (▼) $YBa_2Cu_4O_8$, (△) Y_2BaCuO_5, (▽) $YBa_2Cu_3O_7$, (○) CuO, (●) $BaCuO_2$.

XRD patterns of initial reagent groups 1–4 and 5–8, respectively, at the end of the treatment. After 92 h, 124 is the relevant product of all the initial mixtures with $Cu(NO_3)_2{\cdot}3H_2O$. It must be noticed that the compositions starting with CuO still show some evolution after 572 h we do not exclude that at longer times the reaction product will be 124 with a similar yield to the compositions that started with $Cu(NO_3)_2{\cdot}3H_2O$, but reaction times that approach one month are of little practical interest.

From the analysis of the previous results it is evident that the presence of $Cu(NO_3)_2 \cdot 3H_2O$ is always necessary to obtain the 124 compound in a reasonable time. This seems a striking result, since TG, DTA and X-ray data all show that at 165 °C $Cu(NO_3)_2 \cdot 3H_2O$ decomposes to give $Cu_2(OH)_3NO_3$ as a solid product and at 279 °C this last compound decomposes to CuO. Therefore, whatever makes the presence of $Cu(NO_3)_2 \cdot 3H_2O$ important for the reaction evolution, it must happen during the early stages of the heating-up process. This will be discussed along with the combined results of DTA and XRD analysis performed at the relevant temperatures.

The analysis of the behaviour of the single reagents as temperature increases can give a first explanation. All the nitrates used, when heated, become liquid first and then decompose to oxides; the carbonates and the oxides remain solid in the temperature interval of interest. In particular, $Cu(NO_3)_2 \cdot 3H_2O$ melts at 114.5 °C [14] and it remains liquid until the decomposition process starts at 165 °C. $Y(NO_3)_3 \cdot 5H_2O$ melts at 88 °C, then at 100 °C it starts losing H_2O and at about 240 °C the decomposition process begins, which is accomplished at 518 °C with the total conversion to Y_2O_3. $Ba(NO_3)_2$ becomes liquid at 590 °C and it decomposes to oxide above 750 °C.

The synthesis with the nitrates, being in part carried out in the liquid state, is the one that allows the highest homogeneity; apparently, under the experimental conditions, phase segregation processes are not relevant. Since copper is the element with the highest number in the 124 formula unit, it is not surprising that it is essential for a good result. In fact, it is known that solid-state reactions are usually limited by reagent diffusion and a homogeneous distribution of the reagents significantly favours the reaction evolution.

The analysis of the reaction during the heating-up process can be very complex. In general the DTA measurement of the various reactions shows a very complex peak structure and a proper interpretation is beyond the purpose of the present work. Nevertheless, since the final products depend on the initial steps of the reaction it is also interesting to analyse some elementary reactions that can be identified between the reagents during the first heating step.

Consider first the reactions which have as initial reagent CuO. During the first heating-up process CuO is relatively inert; only high-temperature diffusion-limited reactions are relevant for this compound. When the nitrates of the other elements are present, the various melting and decomposition processes can be identified in the DTA graph (cases 1 and 2). The only chemical reaction, other than decomposition, happens when $Y(NO_3)_3 \cdot 5H_2O$ and $BaCO_3$ are present (case 3). In this case, above 300 °C, there is a reaction that gives $Ba(NO_3)_2$ and Y_2O_3 as solid products. The reaction is not complete because the XRD peaks of $BaCO_3$ are also present. Apparently, the composition of case 3 reduces to that of case 2, so one may wonder why this composition gives better final results. The main difference is that now there is an intimate mix between $Ba(NO_3)_2$ and Y_2O_3, better than in case 2, because, during the reaction, $Y(NO_3)_3 \cdot 5H_2O$ is in the liquid state and it converts to oxide reacting with $BaCO_3$. Finally, in case 4 $BaCO_3$ starts to react with the other oxides at about 800 °C. This reaction is diffusion-limited and it is slow: after 12 h approximately 50% of $BaCO_3$ is still unreacted.

Consider now cases 5–8: the presence of the reagent $Cu(NO_3)_2 \cdot 3H_2O$ changes the initial reaction behaviour in several ways. Above its melting temperature $Cu(NO_3)_2 \cdot 3H_2O$ reacts with $BaCO_3$ (cases 7 and 8) and/or Y_2O_3 (cases 5 and 7) to give $Cu_2(OH)_3NO_3$ and the corresponding nitrates as solid products. Afterwards, at about 279 °C, $Cu_2(OH)_3NO_3$ decomposes to CuO and the reaction follows a similar path as the previous ones (cases 1–4). Actually, the reaction between $Cu(NO_3)_2 \cdot 3H_2O$ and $BaCO_3$ may start during the mixing and milling because the powders are hygroscopic and it may happen even at room temperature if there is enough water to allow ionic mobility. The reaction at low temperatures allows a better homogeneity at the microscopic level because it is partially carried out in the liquid state; even though the liquids are very viscous, capillary forces help the spreading of the liquid in the powder matrix. Actually, the high viscosity of the liquid phase is convenient, because the eventual phase segregation of the solid species is not favoured. In case 5 there are no low-temperature reactions between the initial reagents; the nitrates decompose to give very fine oxide powders.

The initial reaction steps are also relevant to control the presence of impurities whose formation can be explained by a local heterogeneous concentration of reagents. For example, yttrium-rich zones give rise to Y_2BaCuO_5. Unfortunately, under the present procedures, once formed, this compound does not react easily with the other powders to give 124, so improvements have to be developed in the initial reaction stages to avoid the formation of Y_2BaCuO_5.

The resistance measurements show the presence of superconductive material for all the samples under consideration. The onset of the superconductive transition and the zero resistance point differ in a significant way, though. The samples prepared with $Cu(NO_3)_2 \cdot 3H_2O$ have a higher onset (around 70 K). The samples prepared with CuO show the superconductive onset but only reaction 4 reaches zero resistivity (at 40 K). The samples are heterogeneous so we do not give any further interpretation of these measurements.

The present work has considered eight different combinations of starting reagents for 124 synthesis. It clearly indicates that the initial reaction steps are crucial for 124 preparation at low oxygen pressure. It is also shown that several fast enough routes to the synthesis of $YBa_2Cu_4O_8$ are possible at 1 atm oxygen pressure, provided that copper nitrate is present as a reagent.

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